

ANNOTATION

to the series of scientific works «Crystal chemistry of uranium compounds with tetrahedral oxoanions», nominated for the «Scientific Work Award» of St. Petersburg State University at the category «For the Contribution to Science of Young Researchers»,

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Within the last fifteen years, structural chemistry of actinide-containing compounds experienced continuous and extensive development due to both problems of storage and disposal of spent nuclear fuel, and the perspective of fabrication of novel functional materials based on uranium and transuranium elements. By application of a wide range of experimental techniques, synthetic approaches and advanced analytical methods it was possible to identify new classes of actinide-containing compounds, in particular, nanostructures based on uranium, neptunium and plutonium oxides: nanotubules and nanoclusters. However, the field is still far from being mature, and there many ‘white spots’ worth of investigation. Even the structural chemistry of uranium, not to mention transuranium elements, contains many unsolved problems and unanswered questions.

The U^{6+} atoms are present as approximately linear uranyl-ions $[UO_2]^{2+}$, that are coordinated by four, five or six additional anions in the equatorial plane. For the valence saturation of equatorial anions it is necessary to form additional chemical bonds, hence the uranyl polyhedra are usually polymerize with each other only through the equatorial vertices and edges, that results in prevalence of layered structures among the minerals and synthetic uranyl compounds. In addition, uranium compounds containing oxoanions of hexavalent cations (S, Mo, Cr, Se) are of special importance from the environmental and mineralogical points of view.

Some basic principles of uranyl-containing compounds’ crystal structures formation that discussed in the project may be outlined as follows.

In the crystal structures of inorganic uranyl compounds, uranyl selenate and uranyl sulfate complexes are linked via monovalent cations (K^+ , Na^+ , etc.) or octahedrally coordinated divalent cations ($[Ni(H_2O)_6]^{2+}$, $[Zn(H_2O)_6]^{2+}$, $[Mg(H_2O)_6]^{2+}$, etc.).

In the crystal structures of amine-templated uranyl compounds, structure formation is regulated by hydrogen bonding systems and by arrangement of hydrophobic and hydrophilic parts of molecules with voids and dense fragments of inorganic complexes. The proposed “principle of hydrophilic and hydrophobic zones” can be formulated as follows: The hydrophobic zones of an organic complex (a packing or a single molecule) are associated with the space of large hollow rings of an inorganic complex, whereas hydrophilic zones tend to tight aggregates of small rings.

The basic structural principle of organic-inorganic uranyl composites templated by electroneutral molecules (such as crown ethers), is the translation of interactions between organic and inorganic components by means of protonated water molecule complexes (e.g., $H_5O_2^+$ and H_3O^+).

The principle of dimensional reduction was applied to uranyl oxysalts with general formula $A_n(\text{UO}_2)_p(\text{TO}_4)_q(\text{H}_2\text{O})_r$, where A^+ = monovalent cation, and T^{6+} = S, Se, Cr, Mo. Incorporation of monovalent cations and H_2O molecules into the structure would result in the decreasing dimensionality of the UO_2TO_4 unit, and it is in agreement with the principle of dimensional reduction. The specific fields of structural units' different dimensionalities existence have been separated on a UO_2TO_4 – $A_2\text{TO}_4$ – H_2O compositional diagram.

The statistical analysis of the $\text{U}-\text{O}_{\text{br}}-T$ bond angles in the crystal structures showed the possibility for the specification of the undulation of crystal complexes. The local distribution of the $\text{U}-\text{O}-\text{Se}$ links supports the suggestion that the lower $\text{U}-\text{O}_{\text{br}}-T$ angles correspond to the direction of the higher layer undulation: the smallest angles in the structures matches the “wave’s crest”, while the biggest angles stretches along the “wave’s wall”. Another point is that the average angles arranged in the middle part of the interval even for highly distorted layers, which could be explained by the tendency of the layer to flatten itself at least partially.

It is of great interest that natural and synthetic chemistry of compounds containing oxoanions of hexavalent cations are remarkably different. For instance, uranyl selenates are not known yet as minerals but this family of compounds is most representative among the synthetic uranium compounds. And uranyl sulfates are one of the most widespread natural phases that represent secondary uranium mineralization. It is noteworthy that there are several isotypic uranyl sulfates and selenates known, which points out to the possibility of Se^{6+} - S^{6+} substitution in minerals and synthetic compounds. The study of the phase formation in mixed uranyl sulfate-selenate systems seems to be a promising avenue from both geochemical (mineralogical) and chemical points of view. Investigation of the phase formation in the aqueous uranyl nitrate – sulfuric acid – selenic acid – potassium hydroxide system provide some interesting implications for mineralogy and explorative inorganic chemistry of uranium. The results of the study reveal a rather complicated evolution of the structure and composition of crystalline phases in the system under consideration depending upon the changing $\text{Se}:\text{S}$ ratio. A general description of the basic evolutionary trends demonstrated: the absence of a continuous solid solution in the system and the absence of isotypic sulfate and selenate phases. In continuation of studies on the structures of mixed uranyl sulphate-selenates, a system with another alkali metal, Cs, was investigated. As the result, a selective $\text{Se}-\text{S}$ substitution depending on the coordination of the tetrahedral sulfate complex was found.